

Bulletin of National University of Uzbekistan: Mathematics and Natural Sciences

Volume 2 | Issue 3

Article 4

8-8-2019

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Davron Bekchanov

Chirchik State Pedagogical Institute; National University of Uzbekistan, bekchanovdj@gmail.com

Mukhtar Mukhamediev

National University of Uzbekistan; Chirchik State Pedagogical Institute, mmuxamediev@mail.ru

Dilfuza Gafurova

National University of Uzbekistan, d_gafurova@mail.ru

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Recommended Citation

Bekchanov, Davron; Mukhamediev, Mukhtar; and Gafurova, Dilfuza (2019) "Physico-chemical properties new nitrogen- and phosphorus containing ion exchange resins on the base of polyvinylchloride," *Bulletin of National University of Uzbekistan: Mathematics and Natural Sciences*: Vol. 2 : Iss. 3 , Article 4. Available at: https://uzjournals.edu.uz/mns_nuu/vol2/iss3/4

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PHYSICO-CHEMICAL PROPERTIES NEW NITROGEN- AND PHOSPHORUS CONTAINING ION EXCHANGE RESINE ON THE BASE OF POLYVINYLCHLORIDE

BEKCHANOV D. J.^{2,1}, MUKHAMEDIEV M. G.^{1,2}, GAFUROVA D. A.¹

¹*National University of Uzbekistan, Tashkent, Uzbekistan*

²*Chirchik State Pedagogical Institute, Chirchik, Uzbekistan*

e-mail: bekchanovdj@gmail.com, mmuxamediev@mail.ru, d_gafurova@mail.ru

Abstract

Peculiarities of the interaction of PPE-1 anion exchange resin with phosphonic acid production based on granular polyvinyl chloride were studied. As a result of the modification, a polyampholite was obtained in terms of physico-chemical properties not inferior to the industrial polyampholite APFC-45. We also investigated the sorption of copper (II), nickel (II) and indium (III) ions on a polyampholite based on granular polyvinylchloride. The dependence of static adsorption on aqueous solutions on the concentration of metal ions and the temperature of the system is established. Isotherms were constructed and found the adsorption equilibrium constants, the thermodynamic parameters of the process - isobaric - isothermal potential (ΔG), enthalpy (ΔH) and entropy (ΔS). It is shown that the investigated sorbent absorbs ions Cu (II) to a greater extent than the other ions.

Keywords: nitrogen and phosphorous containing polyampholite, sorption, ions of copper, indium and nickel, chemisorption and thermodynamic parameters.

Introduction

To solve the technological problems associated with obtaining high-purity substances in separation processes, extraction and concentration of rare and non-ferrous metals should be used chelating resins having a greater affinity for the studied ions. Such sorbents include nitrogen and phosphorus polyampholytes having in its composition and amino phosphonic group [1]-[4]. Such sequestering polymers may be used in non-ferrous metallurgy, hydrometallurgy for recovery of indium, copper and nickel from waste water in the chemical industry, and also for producing substances of various natures.

Polymetallic ores, in addition to the target metals, contain a large number of related impurities, so when they are leached, aqueous solutions of complex composition with low metal concentrations are formed. Many enterprises use outdated technologies and have a low level of mechanization and automation, as a result of which the content of heavy metals in wastewater is very high. In this regard, it is urgent to improve sorption processes in the processing of productive solutions of mining and processing plants for the concentration and separation of valuable components and

the treatment of industrial wastewater from heavy metal ions [5]-[8]. This can be achieved using ion exchange and sorption methods for processing aqueous solutions.

In various wastewaters, the amount of metals varies widely. Copper is one of the standardized mineral components; its presence in natural, waste, water and boiler water is regulated at the MAC level. For copper, the MAC in drinking water is 1.0 mg/g. At the same time, 60-120 mg/l is contained in acidic effluents of non-ferrous metal processing plants, and 80-100 g/l of copper in the exact waters of galvanic shops. In the wastewater of nickel plots, the nickel concentration is 0.5 g/l [9]-[11]. At the same enterprise with a complex technological cycle, wastewater can be completely different in composition. So saline, the nickel production runoff contains 50 g/l H_2SO_4 and 200 mg/l copper, and the waste water from the pyro metallurgical processes contains 0.5-1.0 mg / l nickel and 0.1 mg / l copper. During heap leaching of oxidized and mixed ores of the Kalmakyrsk deposit with a solution containing 6.75 g/l H_2SO_4 . Industrial solutions contain 1.47-3.83 g/l of copper [12].

In the group of chelating ion exchangers containing phosphonic and aminophosphonic functional resins with the addition of aminoalkylphosphonate functional groups, such as Duolite C-467, Duolite ES-467, Lewatit OC 1060, Purolite S 940, Purolite S 950 and Chelite P occupy a significant place. In the sorption of heavy metal ions on such chelate ion exchangers, the following affinity is obtained: $Pb^{2+} > Cu^{2+} > UO_2^{2+} > Zn^{2+} > Al^{3+} > Mg^{2+} > Sr^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Na^+ > Ba^{2+}$. These ion exchange resins, as well as the previously mentioned phosphonic ones, exhibit a weak affinity for Ca (II) and Mg (II) [13]-[15].

In [14], it was found that Duolite ES-467 has a higher ability for copper (II) ions compared to nickel (II) and iron (III) and that the capacity decreases with decreasing pH and the concentration of metal ions in solution. In addition, Duolite ES-467, Purolite S 950 has been proven to have high affinity for various heavy metal ions and is successfully used in metallurgical and waste water treatment processes. A serious drawback of the extraction of indium carriers containing iminodiacetic groups is a need for sorption at pH "1.5 at which these sorbents have the greatest selectivity for indium, which significantly complicates the technology of extracting indium from real technological solutions [5]. Similarly to the significant disadvantages of this class include low capacity adsorbents with respect to indium (0.184 mmol / g) in the conditions of maximum selectivity (70-80%).

Complexing sorbents useful for the selective adsorption of indium can be divided into two classes: the sorbents containing iminodiacetic groups and sorbents containing phosphonic groups [15]-[17].

Sorbents second class containing phosphonic groups can be divided into carriers having in its composition aminomethylphosphonic, monophosphonic and gemdiphosphonic groups [16].

The advantages of the second class of sorbents can be attributed to their relatively high capacity and selectivity to indium in the less acidic solutions ($pH \sim 4$). This fact is most pronounced for gemdiphosphonic sorbents containing functional groups, such as carriers Diphonix Resin (Eichrom Industries) obtained by copolymerization of acrylonitrile, divinylbenzene, styrene and phosphorus containing monomer, followed

by hydrolysis and sulfonation of the resulting product. The disadvantages of this method are: a reduced selectivity for indium, the complexity and multi-stage production process, the long duration of the production cycle, the use of expensive and not readily available phosphorus-containing monomer required for the introduction of gemdifosfonovyh groups [17].

Therefore, in [18] offered a method for producing a complexing sorbent for the selective extraction of indium, having in its composition gemdiphosphonic functional groups. Introduction of the gemdiphosphonic functional groups is accomplished by treating the spherical crosslinked macroporous copolymer of acrylonitrile and divinylbenzene with concentrated phosphoric acid at a temperature $140-160^{\circ}\text{C}$ within 13-35 hours. The same process, in the presence of a diluent (chlorobenzene), carried out at a temperature $100-130^{\circ}\text{C}$. The maximum value for S indium ions (III) when removed from the concentrated solution of indium sulphate (7.489 g/l) was 2.9 mg-equivalent/g. The selectivity of the sorbent in the presence of indium ions in the accompanying technological solutions was 90%.

To extract ions nickel (II) used as phosphorus-containing resins. The authors [19] for the sorption of nickel (II) ion exchanger was used, based on the polymer industry - butadiene rubber stamp SKD. The ion exchanger obtained by the reaction of oxidative chlorophosphorylation ACS under the PCl_3 in the presence of oxygen, followed by hydrolysis of the resulting product. The laws of kinetics of sorption of cobalt and nickel on a phosphorus-containing cations is investigated. The results obtained revealed that the rate-limiting step in the process is both external and internal diffusion. At the same time, a contribution to the overall speed of the process of making and stage interaction sorbed ions with functional groups of the cation exchanger. This SEC cation exchanger of ions nickel (II) is very small and is 0.5 mmol / g. This low capacity due to the absence of likely complexing groups in the cation resin.

The paper [20] presents the results of studying the process of sorption of nickel and cobalt ion exchanger based on hydrolyzed polyacrylonitrile (GIPAN) and epichlorohydrin. The influence of the conditions for obtaining the resin: temperature of reaction, the ratio of the starting materials and solvent nature - the process of sorption of these ions is investigated. It is shown that in the process modification GIPAN epichlorohydrin formed polyampholyte complexing with ammonium and carboxyl groups in the side chain. The presence of complexing groups results in a higher value compared with the CDE and SKD it is around 1.8 mmole.eqv /g.

The authors [21]-[25] studied the ion exchange process for the exchange of ions of heavy metals (Cu^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , and Co^{2+}) and the ions Ca^{2+} , Na^{+} , and NH_4^{+} with two commercially available ion exchange chelating resins aminophosphate functional groups (Purolite S 940 and S 950). Evaluation of the results of sorption by surface complexation theory led to a set of binary equilibrium parameters that remain the same in multicomponent systems. With the analysis of the kinetic parameters of the secondary, tertiary and quaternary equilibrium and balance of complex agents in the wastewater produced in the processing of metal surfactants have been proposed based on equations that calculated theoretical values of sorption and compared with

experimental data. In all cases it was found significant matching.

In [26], the authors conducted a study on the extraction of trace amounts of heavy metals by ion exchange. Experiments were made using ion exchange resin Lewatit CNP 80 (weakly acidic) and Lewatit TP 207 (slightly acidic and chelate). It is investigated the effect of pH, time, metal concentration and the amount of the ion exchanger in the sorption process. Studied chelate media showed a high and more rapid sorption capacity for metal ions such as ions of lead (II), copper (II), zinc (II), Cd (II) and Ni (II). The optimum pH range for the ion exchange of the above metal ions on Lewatit CNP 80 and Lewatit TP 207 were 7.0-9.0 and 4.5-5.5, respectively. The data show that the nitrogen and phosphorus containing ion exchanger physico-chemical and sorption properties selective with respect to ions Cu (II), Ni (II) and In (III) to form stable complexes with them. Therefore, the present work is devoted to the analysis of sorption of Cu (II), In (III) and Ni (II) from aqueous solutions of nitrogen and phosphorus containing polyampholyte PPE-1-P.

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The data show that the nitrogen and phosphorus containing ion exchanger physico-chemical and sorption properties selective with respect to ions Cu (II), Ni (II) and In (III) to form stable complexes with them. Therefore, the present work is devoted to the analysis of sorption of Cu (II), In (III) and Ni (II) from aqueous solutions of nitrogen and phosphorus containing polyampholyte PPE-1-P.

1 Preliminary results

Obtaining of PPE-1-P polyampholite: In a 250 ml flask equipped with a reflux condenser, 25 grams of PPE-1 anion exchange resin based on granular PVC were placed [18] and this flask was added with a 50% aqueous solution of phosphonic acid, heated at a temperature of 373 K for 8 ocloc'k. The product was filtered and washed with distilled water until neutral and dried to constant weight. The spectra of the samples were recorded using an IRTracer-100 SHIMADZU IR-Fourier spectrometer (Japan) complete with a single ATR attachment with a diamond / ZnSe MIRacle 10 prism, designed to analyze solid, liquid, pasty, gel-like substances in the scanning range: 4600-600 cm^{-1} . SEM - on an EVO MA-10 scanning electron microscope (Carl Zeiss, Germany) equipped with a microanalytical system for energy dispersive X-ray (EDX) microanalysis (Oxford Instruments, UK) that allows to detect all chemical elements starting from boron.

Working solutions of copper nitrate, indium nitrate and nickel nitrate was prepared by dissolving the sample $\text{Cu}(\text{NO}_3)_2$, $\text{In}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ a certain amount of distilled water. The pH of the solution was adjusted using ammonium acetate buffer solution. We study the dependence of the adsorption of metal ions on the time, temperature and concentration of solutions. The concentration of ions In (III) in solution was measured by conductivity meter CAL-1M2, pH of the solution was measured using a universal ionomer EV-74 and pH-meter pH / mV / TEMP Meter P25 EcoMet. The change in concentration of ions Cu (II), and Ni (II) in solution was measured by the spectrophotometric method. The change in optical density of the solution was measured with a microplate reader Enspire Perkin Elmer (USA).

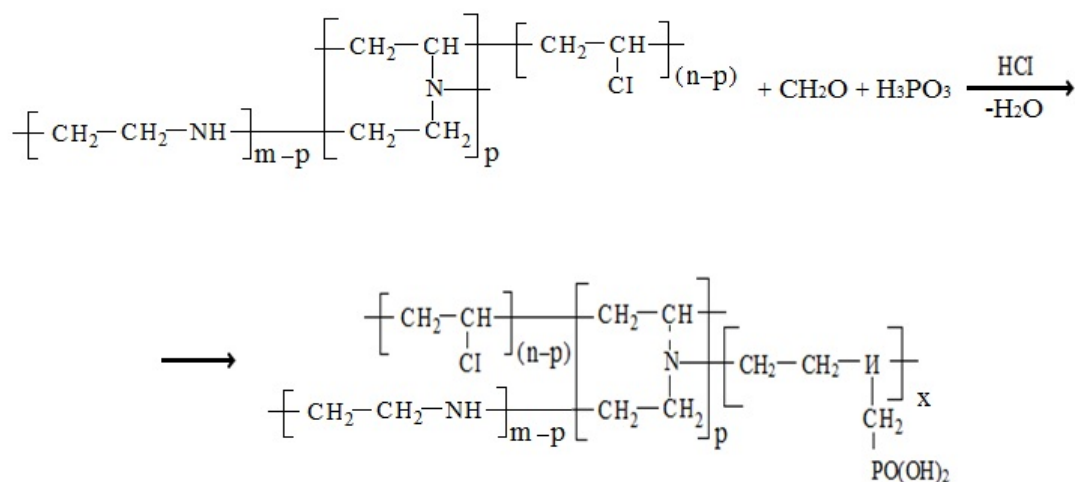
2 Main results

In this work, the synthesis of ion-exchange polymer material and the study of their physicochemical and sorption properties remains an urgent task. Complexing materials are obtained mainly: by polymerization and copolymerization of monomers containing various functional groups and by chemical transformations of the finished polymers. Among these methods, the latter is of particular interest, since this method can be used to obtain ion exchange resin in a one-step chemical reaction.

The phospholation reaction was carried out in a 25% aqueous solution of phosphite acid at different ratios of the polymer base modifying reagent, temperatures: 60°C ; 70°C , 80°C , 90°C , 100°C , 110°C , and during 2, 4, 6, 8, and 10 hours. The resulting products were washed with water, dried to constant weight, and their physicochemical parameters were determined. With an increase in the concentration of the modifying reagent in the system to 55%, the yield of the product increases; with a further increase in the yield of the final product, it remains constant [27].

Below is the reaction scheme for the modification of PPE-1 anion exchanger with phosphonic acid.

To identify the obtained polyampholite, IR spectroscopic studies were performed. In fig. 1, 2 presents the IR spectra of the initial and obtained ion exchangers.



The data of IR spectroscopic studies (Fig.1, 2) confirm the presence in the structure of nitrogen-phosphorus-containing polycomplexes of phosphonic and amide groups. In the IR spectra, quite intense absorption bands were found in the region of 960 and 1080 cm^{-1} , characterizing the $P(O)(OH)_2$ bonds, and also a band in the region of 1170 cm^{-1} , characterizing the stretching vibrations of the bond. The band in the region of 1640 cm^{-1} can be attributed to the absorption of the carbonyl group in amides; the band in the region of 1560 cm^{-1} characterizes the deformational vibrations of the bond = N-H. The presence of a wide absorption band in the region of 2800-2850 cm^{-1} , characterizing salts of secondary and primary amines, indicates the existence of aminomethylene phosphonic groups in polycomplexes in the form of an internal salt [28].

Qualitative and quantitative elemental analysis of the polymer obtained by phospholating anionite PPE-1 shows that the polyampholyte contains 2.32% O, 4.3% N and 1.5% P in its composition. These data confirm the presence of nitrogen and phosphorus-containing groups in the composition of the obtained polymer.

As can be seen from Figure 3, the rate of phospholation reaction directly depends on the concentration of phosphinic acid, which indicates the ratio of this reaction to ordinary reactions of the first degree. From figure 3, the value of the order of the reaction for phosphite acid was calculated equal to 1,43 and, accordingly, the equation of speed of this reaction will look as follows:

$$V = K[H_3PO_3]^{1,43}$$

The effect of temperature on the modification reaction was positive up to 100 $^{\circ}\text{C}$ (Table 2). Apparently, with an increase in temperature due to an increase in the Brownian motion of molecules, the probability of interaction of reagents increases. Since the modification reaction was carried out in open systems, an increase in temperature above 100 $^{\circ}\text{C}$ does not affect the course of the reaction.

Thus, by the modification of PPE-1 anion exchanger with phosphorous acid, granular nitrogen and phosphorus containing polycomplexon are obtained. The kinetics of

the production process was studied and the most favorable conditions for its preparation were found - the duration of the phosphorylation reaction is 8 hours, the reaction temperature is $90 - 100^{\circ}\text{C}$, the concentration of phosphorous acid is 55%, the molar ratio of the components is 1: 2.

Chemical resistance: To determine the chemical resistance, the ion exchanger was exposed to strong oxidizing agents, various acids and bases. To do this, the studied polyampholyte was left in different reagents for 10-48 hours. Then, the samples of the ion-exchange material were filtered off, washed to a neutral medium, and dried to constant weight. The quality control of the sorbent after exposure to various aggressive reagents was carried out by determining the SEC of the ion-exchange material. The results on the stability of the obtained polycomlexon to various aggressive environments are shown in table 3. For comparison, table 3 also shows the data on the effects of these reagents on industrial nitrogen and the phosphorus-containing sorbent APFC-45, which is a copolymer of vinylpyridine and phosphorus-containing monomer CF-5.

From the above data it can be seen that the polyampholyte synthesized by us in its chemical resistance fully meets the requirements and can find application in industry.

The absorption isotherm of water steam was studied in order to calculate specific surface area of produced polymer materials. Because the absorption isotherm of polymers was S-shaped, the BET formula has been used for calculation.

In Table 4 parameters of capillary-porous structure of PVC and PPE-1 and PPE-1-P sorbent are given. It is clear from the table that by transferring from PVC to PPE-1 and PPE-1-P the sorption (X_m , g/g), specific surface of polymers (S_{rel} , m^2/g), size of pores (r_k , \AA) and the total volume of pores increase, this process has been explained by a change of PVC supramolecular structure during modification process.

The resistance of PPE-1 anionite and PPE-1-P polyampholite, synthesized from granular PVC, to various reagents as well as the solutions of powerful oxidizer, strong acids and strong bases has been studied.

To evaluate the heat resistance of ion exchangers, the ion-exchange material is heated to a high temperature and the initial exit time of a low molecular weight compound is determined during thermal or thermal oxidative degradation. To evaluate the heat resistance of ion exchangers, the thermogravimetric (TG) method is used; it is based on weight loss depending on temperature.

As can be seen from Figure 4 for the PPE-1 anion exchanger obtained on the basis of polyvinyl chloride, due to the moisture content, a sharp increase in mass loss is observed to a temperature of 130°C , then with prolonged heating to 240°C the sorbent remained stable and did not undergo thermal degradation, however, upon further heating, the loss mass of anion exchange resin is gradually increasing.

The TG analysis and DSK curves of polyampholyte PPE-1-P show that the polymer matrix has thermal resistance up to a temperature of 230°C . As can be seen from the DSK curves at 192°C , an exothermic peak with a reaction energy of 49.87 J/g is observed. This peak is most likely due to the complemented chemical interactions observed between the already bound PVC and PEPA macromolecules.

According to the results of thermogravimetric analysis, it can be noted that for PPE-1 anion exchange resin and PPE-1-P polyampholite obtained on the basis of polyvinyl chloride up to temperatures of 180-230°C, a slight weight loss is observed. Therefore, these ion-exchange materials even at high temperatures retain their common component and have high thermal stability.

Sorption properties of polyampholite

PPE-1-P ion exchange material contains in its composition phosphonic group therefore studied metal cations sorption occurs due to the electrostatic binding of these metal ions of these functional groups. The presence of amino groups in the resin composition also promotes the binding of metal ions due to chelating. The degree of binding of ions depends on the degree of ionization of the functional groups of the ion exchange material, and that in turn depends on the pH. Therefore, according to a study on the sorption of the studied metal ions were carried out on the pH media.

Figure 5 shows the sorption of copper, indium and nickel ions on dependence of pH in water solution. As seen from the graph, the maximum sorption of ions of copper, indium and nickel is held in a weak acid medium. The high degree of sorption of Cu (II) and In (III) was observed at pH = 6.28 and ions and Ni (II) at pH = 4.8. Further studies were carried out with solutions of ions Cu (II), In (III) and Ni (II) have found the optimal pH.

Figure 6-8 shows the sorption isotherm ions Cu (II), In (III) and Ni (II) by PPE-1-P at different temperatures. As can be seen from the figures increasing concentrations of copper (II) nickel (II) and indium (III) ions and the temperature rise in the initial solution results in increased sorption. In this SEC of synthetic solutions for copper ions (II) nickel (II) and indium (III) are as these values are not inferior to known ion exchangers.

It is known that heterogeneous chemical processes of addition and substitution proceeding involving a fixed number of functional groups, when considered on the basis of the law of mass action equations are characterized by having a "Langmuir" properties [29].

Usually, to find the value of K and A_{∞} Langmuir equation leads to the following form:

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{B}{A_{\infty}} \cdot \frac{1}{C}$$

$B = 1 / K$. Plotted $1 / A$, $1 / C$, the slope of the straight line gives the value of B/A_{∞} and intercept on the y-axis value of $1 / A_{\infty}$. The dependence of $1/T$, $1/C$ process for sorption of copper ions (II) nickel (II) and indium (III) sorbent at various temperatures. We see that this dependence is a straight character, indicating the submission of the sorption theory of Langmuir monolayer,

Thermodynamic functions were identified by us from the dependence of equilibrium constants on the temperature. Based on the fact that $\Delta G = \Delta H - T\Delta S$ the values found ΔH and ΔS .

For this $R\ln K$ plotted versus $1/T$, the slope of this line is calculated ΔH , ΔS calculated from equation $\Delta S = \frac{\Delta H - \Delta G}{T}$ [29].

The calculation results are shown in Table 5.

Analysis of the data of Table 1 shows the spontaneous nature of the process. As seen from Table sorption of metal ions is increased in the following order: $In(III) < Ni(II) < Cu(II)$. The data show that with increasing temperature the sorption is increased sorption process proceeds with a decrease in free energy, enthalpy and entropy of the system, which indicates the nature of the ion exchange process of sorption.

The evaluation of the stability constants of the surface complexes formed during the sorption of copper (II), nickel (II) and indium (III) with nitrogen and phosphorus-containing groups sorbents that ions Cu (II) to form more stable complexes with the functionalized sorbents compared with other ions studied.

3 Conclusions

Using IR spectroscopy, elemental and thermal analysis, and analytical methods, the structure of the obtained anion exchangers and polycomplexes based on granular polyvinyl chloride has been proved and their chemical and thermal stability has been established.

In the laboratory condition for the obtained polyampholyte, the basic physico-chemical properties established in the state standard were studied and comparing them with the properties of competing ion exchangers it was shown that the polyampholyte we obtained was not inferior to the polyampholyte used in industry.

A study of the kinetics and thermodynamics of the extraction of Cu (II), Ni (II) and In (III) ions by a polycomplexon based on granular polyvinyl chloride has established the order of sorbent selectivity with respect to non-ferrous metals, which has the following form: $Cu(II) > Ni(II) > In(III)$.

4 Tables and Figures

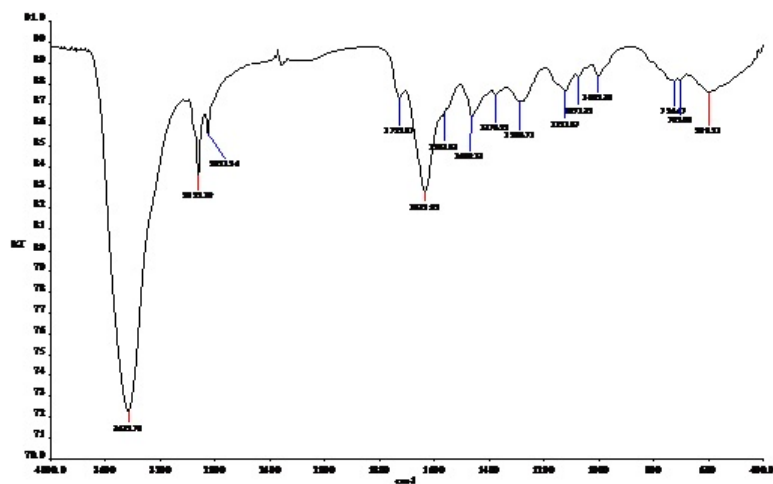


Figure 1. IR spectra of PPE-1 anion exchange resin

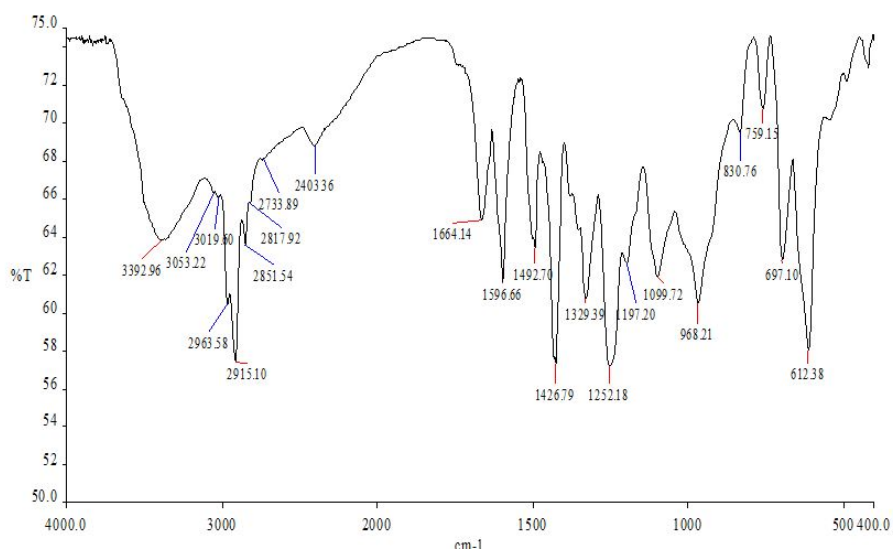


Figure 2. IR - spectra of polyampholite PPE-1-P

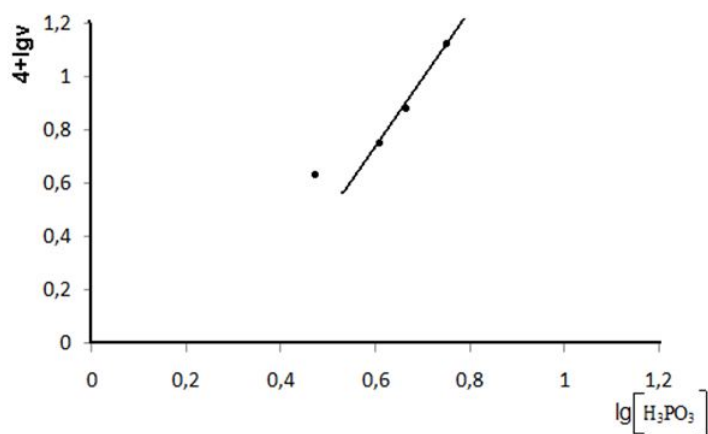


Figure 3. The dependence of the rate of phosphorylation of anion exchanger PPE-1 on the concentration of phosphite acid.

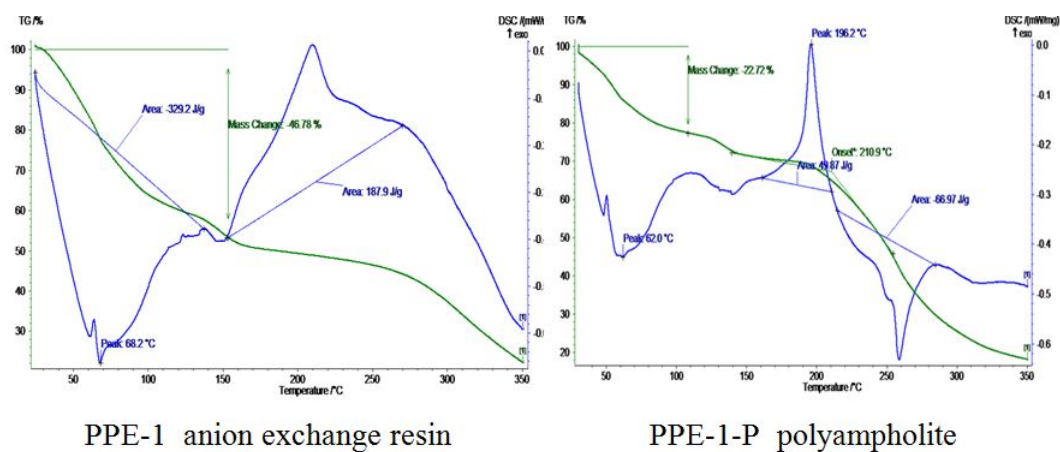


Figure 4. Dervitogram of polymeric materials

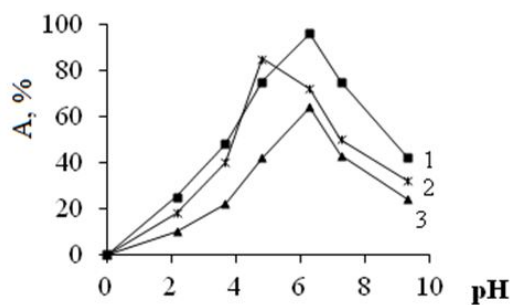


Figure 5. Relative sorption of Cu^{2+} , (1) Ni^{2+} (2) and In^{3+} (3) on dependence of the pH

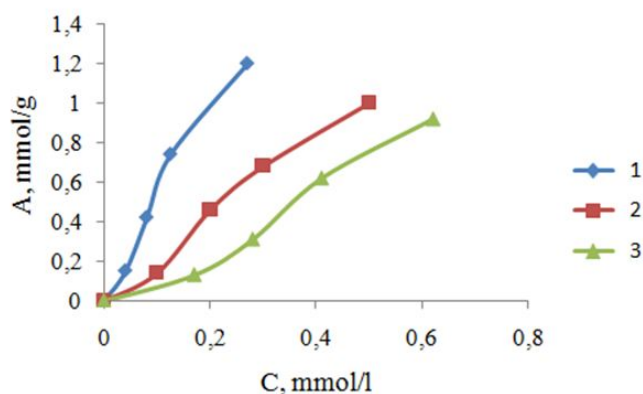


Figure 6. Adsorption isotherms of Cu^{2+} ions with an ion exchanger material PPE-1-P at different temperatures. 1, 2, 3 temperature sorption 313, 303, 293K, respectively

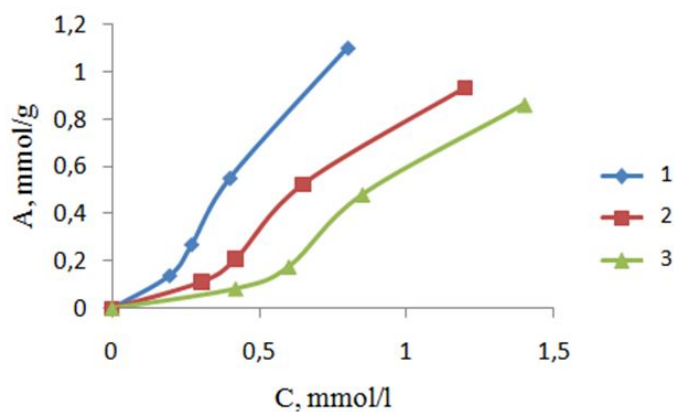


Figure 7. Adsorption isotherms ions Ni^{2+} with PPE-1-P ion exchanger at different temperatures. 1, 2, 3 temperature sorption 313, 303, 293K, respectively

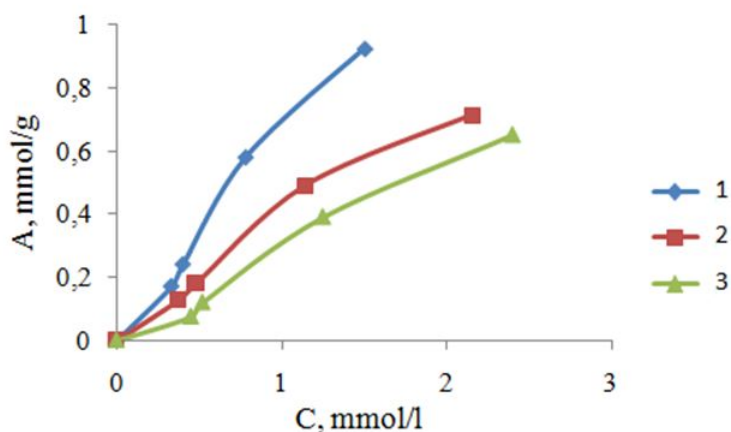


Figure 8. The isotherms of adsorption of ions In^{+3} by PPE-1-P ion exchanger at different temperatures. 1, 2, 3 temperature sorption 313, 303, 293K, respectively

Table 1. Qualitative and quantitative analysis of elements in the composition of polyampholite PPE-1-P

Polymer	Mass fraction of elements in the composition of the polymer, (%)					
	C	Cl	H	N	P	O
PPE-1-P	69,8	13,38	8,7	4,3	1,5	2,32

Table 2. The effect of temperature on the chemical modification of the PPE-1 sorbent with phosphonic acid

Temperature °C	m ₁ gr. before reaction	m ₂ gr. After reaction	Weight gain, %
60	1,0	1,0	-
70	1,0	1,25	25
80	1,0	1,48	48
90	1,0	1,53	53
100	1,0	1,65	65
110	1,0	1,65	65

Table 3. Chemical resistance of PPE-1-P and APFC-45 ion exchangers to various aggressive reagents

Setting	Study conditions		SEC, mg-ekv/g		$\frac{SEC_{before}}{SEC_{after}}$, %	Mass change; %
	T, K	hour	before	after		
APFC-45 (4-VP +CF-5)						
1%HNO ₃	298	48	1.29	2,32	51.8	1.3
5%HNO ₃	298	48	1.62	2,32	78.8	-
1%HCIO ₄	298	48	0	2,32	0	17.2
5%HCIO ₄	298	48	0	2,32	0	17.4
5%NaOH	373	10	2.00	2,32	96.0	-
PPE-1-P (PPE-1+H ₃ PO ₃)						
1%HNO ₃	298	48	3,96	4,20	94,3	2,80
5%HNO ₃	298	48	3,62	4,20	86,6	3,75
1%HCIO ₄	298	48	3,60	4,20	85,7	2.84
5%HCIO ₄	298	48	3,03	4,20	72,1	4.20
5%NaOH	373	10	3.91	4,20	93,1	2,10

Table 4. Change parameters of capillary-porous structures of polymer samples

Sample	PVC	PPE-1	PPE-1-R
Xm, g/g	0,0019	0,0157	0,0189
S _{rel} , m ² /g	6,86	55,13	66,45
W ₀ , cm ³ /g	0,010	0,089	0,014
r _k , Å	29,15	32,28	42,13

Table 5. Constants and basic thermodynamic characteristics for sorption of copper ions (II), nickel (II) and indium (III), ion exchanger PPE-1-P

Metal ions	T, K	A _∞ , mmol/g	Adsorption constant K, l/mmol	-ΔG, J/mol	-ΔH, J/mol	-ΔS, J/mol·K
Cu ²⁺	293	3,05	9,28	4385	12500	13,8
	303	3,32	14,0	4892		28,2
	313	3,85	21,7	6038		29,7
Ni ²⁺	293	2,25	6,35	3590	11500	13,0
	303	2,48	8,43	4310		25,0
	313	2,74	10,84	4597		25,8
In ³⁺	293	1,85	4,18	2170	11200	11,85
	303	2,12	6,54	3127		21,6
	313	2,36	8,45	3969		23,1

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